

PROCESS FOR PRODUCING POLYESTER ARTICLES HAVING LOW ACETALDEHYDE CONTENT

Publication number: EP0842210

Publication date: 1998-05-20

Inventor: NELSON GREGORY WAYNE (US); NICELY VINCENT ALVIN (US)

Applicant: EASTMAN CHEM CO (US)

Classification:

- international: **C08J3/12; C08G63/78; C08G63/88; C08G63/90; C08J3/20; C08J3/12; C08G63/00; C08J3/20; (IPC1-7): C08G63/90**

- european: **C08G63/88; C08G63/90**

Application number: EP19960926190 19960731

Priority number(s): WO1996US12504 19960731; US19950509845 19950801

Also published as:

WO9705186 (A1)
US5648032 (A1)
EP0842210 (A0)
BR9609745 (A)
EP0842210 (B1)

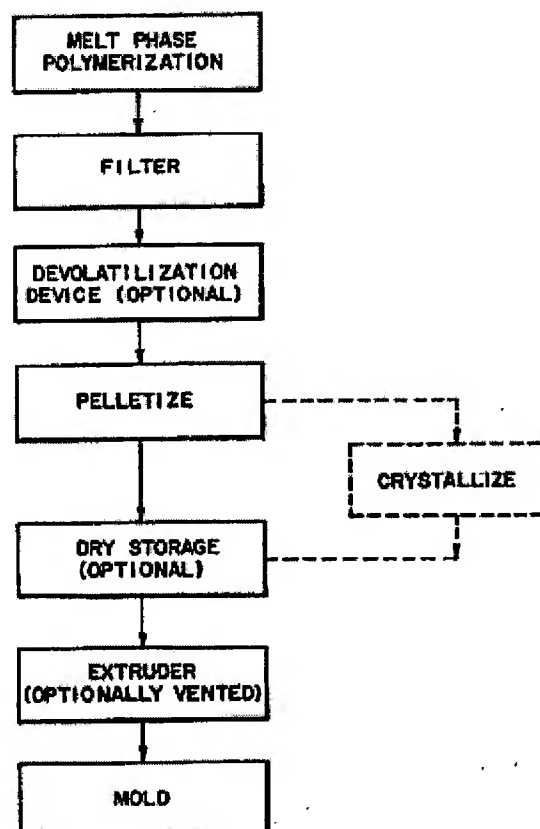
more >>

[Report a data error here](#)

Abstract not available for EP0842210

Abstract of corresponding document: **WO9705186**

Disclosed is a process for producing molded polyester articles having a low acetaldehyde content comprising the steps of: a) reacting a glycol and a dicarboxylic acid in the melt phase to form a polyester having an I.V. of 0.65-0.85; b) solidifying and pelletizing said polyester; c) remelting said polyester in an extruder; and d) forming said polyester into shaped articles, wherein the polyester is devolatilized during or following said polymerization in the melt, while it is being remelted, after remelting, or any combination by passing a purge gas over said molten polyester.



Data supplied from the **esp@cenet** database - Worldwide

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08G 63/90	A1	(11) International Publication Number: WO 97/05186 (43) International Publication Date: 13 February 1997 (13.02.97)
(21) International Application Number: PCT/US96/12504 (22) International Filing Date: 31 July 1996 (31.07.96) (30) Priority Data: 08/509,845 1 August 1995 (01.08.95) US (71) Applicant: EASTMAN CHEMICAL COMPANY [US/US]; 100 North Eastman Road, Kingsport, TN 37660 (US). (72) Inventors: NELSON, Gregory, Wayne; 204 Park Ridge Court, Kingsport, TN 37664 (US). NICELY, Vincent, Alvin; 2605 Suffolk Street, Kingsport, TN 37660 (US). (74) Agent: HARDING, Karen, A.; P.O. Box 511, Kingsport, TN 37662-5075 (US).		(81) Designated States: AU, BR, BY, CA, CN, CZ, HU, IL, JP, KR, MX, NO, NZ, PL, RU, SG, SK, TR, UA, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: PROCESS FOR PRODUCING POLYESTER ARTICLES HAVING LOW ACETALDEHYDE CONTENT (57) Abstract <p>Disclosed is a process for producing molded polyester articles having a low acetaldehyde content comprising the steps of: a) reacting a glycol and a dicarboxylic acid in the melt phase to form a polyester having an I.V. of 0.65-0.85; b) solidifying and pelletizing said polyester; c) remelting said polyester in an extruder; and d) forming said polyester into shaped articles, wherein the polyester is devolatilized during or following said polymerization in the melt, while it is being remelted, after remelting, or any combination by passing a purge gas over said molten polyester.</p>		

```

graph TD
    A[MELT PHASE POLYMERIZATION] --> B[FILTER]
    B --> C[DEVOLATILIZATION DEVICE (OPTIONAL)]
    C --> D[PELLETIZE]
    D --> E[CRYSTALLIZE]
    D --> F[DRY STORAGE (OPTIONAL)]
    F --> G[EXTRUDER (OPTIONALLY VENTED)]
    G --> H[MOLD]
  
```

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

- 1 -

PROCESS FOR PRODUCING POLYESTER
ARTICLES HAVING LOW ACETALDEHYDE CONTENT

Technical Field

5 The present invention relates to a process for
producing polyester articles having low acetaldehyde
content wherein the conventional solid state
polycondensation step is not required. The steps of the
present invention include polymerization in the melt,
10 pelletizing, optionally crystallizing, remelting, and
forming into useful articles, wherein the polyester is
devolatilized during or following polymerization in the
melt, or during remelting.

15 Background of the Invention

 Polyesters are widely used in the manufacture of
fibers, molded objects, films, sheeting, food trays, as
well as food and beverage containers. These polymers
are generally made by batch or continuous melt phase
20 polycondensation reactions well known in the art. The
polymers are then pelletized and used in various
extrusion or molding operations. In certain
applications where higher molecular weight polymers are
required, the pellets are subjected to "solid state"
25 polycondensation conditions in which the inherent
viscosity (I.V.) value is significantly increased. Such
solid state polycondensation reactions are used for two
reasons. First, because the melt viscosity of polyester
polymers is quite high for polymers having I.V. values
30 greater than 0.6, solid stating provides a convenient
means to handle the polymer. Secondly, the solid
stating process provides conditions conducive to
removing unwanted volatile impurities such as
acetaldehyde which is important in some applications as
35 discussed below. Also, polyesters are well known to be

- 2 -

degraded by small amounts of moisture when they are melt processed in conventional equipment. Consequently, polyesters are usually carefully dried to very low moisture levels in a drier prior to melt processing.

5 The drying process may remove some objectional volatile materials other than water also.

During the preparation and processing of polyesters such as poly(ethylene terephthalate) (PET) in the melt phase, certain byproducts are formed. One such
10 byproduct is acetaldehyde, and its presence in molded objects such as food containers, beverage bottles, water bottles, and the like is quite deleterious from a taste standpoint. Particularly for sensitive beverages such as cola, beer, and water, it is highly desirable to
15 produce preforms having less than 10 ppm of acetaldehyde. Achieving this low level of acetaldehyde is difficult, however, because, as is well known to practitioners of the art, acetaldehyde is continually formed as a byproduct during the polymerization and
20 subsequent melt processing of PET and similar polymers.

Before the discovery of the present invention, therefore, a four-stage process has been universally used to provide polyester polymers suitable for uses in which it is important to minimize the presence of
25 acetaldehyde. Such a process typically involves the preparation of a relatively low molecular weight precursor polymer, having an I.V. value of 0.3-0.6, by melt-phase polymerization techniques that are well known in the art. The acetaldehyde content of such a
30 precursor may range from 30 ppm to over 150 ppm, depending on the reaction conditions chosen. This precursor is then cooled, shaped into pellets, crystallized, and subjected to further solid-state polymerization at a lower temperature. Typically, a gas
35 is used to strip glycols, acetaldehyde, and other

- 3 -

reaction byproducts from the pellets so that at the end of the solid-state process, the I.V. value has been increased to 0.75 or more, and the acetaldehyde content has been reduced to below 1 ppm or less. After solid
5 stating, polyesters are commonly handled in contact with ambient air from which it absorbs moisture. Thus, as a third step, the polymer is usually dried immediately prior to the fourth step in which it is heated and melted in order to be formed into a useful shape, such
10 as a beverage bottle preform. The processing typically causes a small decrease in the I.V. of the polymer and an increase in acetaldehyde content of from less than 1 ppm in the pellets, to up to 8 or 10 ppm or more in the shaped article. This dramatic increase in acetaldehyde
15 occurs despite the fact that the molding process takes typically less than one or two minutes to complete.

We have now discovered a process whereby polyesters such as PET and similar polymers may be prepared and used without need for the solid stating process nor the
20 usual drying of solid pellets. The polymer is prepared and used by a combination of the following operations: melt polymerization, pelletizing, optionally crystallizing, remelting, and forming into useful articles, wherein the polyester is devolatilized during
25 or following polymerization in the melt, while being remelted, after remelting, or any combination thereof. A preferred combination of operations would be to prepare the polymer in the melt to the desired I.V., pelletize the polymer, store and/or transport the
30 amorphous polymer pellets, melt the polymer in a machine designed to dry the polymer while melting it or shortly after melting therein preserving the I.V. of the polymer, devolatilize the melt of acetaldehyde, and forming the purified polymer melt into useful shaped
35 articles, such as for example beverage bottle preforms,

- 4 -

wherein the shaped articles having surprisingly low acetaldehyde content. Not only does the process of the present invention avoid the costly additional steps of the conventional process of drying, crystallizing, and solid-state polymerization, but the shaped articles produced by our process possess in addition to low acetaldehyde content, other superior properties such as for example better color, less loss of molecular weight due to breakdown, and freedom from defects known as "bubbles" and "unmelts" which are sometimes formed during the conventional molding process. These and other advantages of the present invention will become apparent in the description which follows.

We are not aware of any prior art which describes the full process of this invention. The following documents may be of interest with respect to certain aspects of the invention.

U.S. Patent 4,430,721 describes PET copolyesters containing 1.5-7.5 mol % of modifying dibasic acids or glycols which have an acetaldehyde content of less than 1.25 ppm.

Japan Patent Application 53-71162 (1978) describes remelting polyester chips and holding the molten polymer under vacuum to reduce the concentration of acetaldehyde.

U.S. Patent 4,263,425 describes the solid stating of PET pellets to provide polymer having a low concentration of acetaldehyde. This reference also states: "Acetaldehyde can partially be eliminated if a stirred melt is treated at higher temperatures under vacuum. By this method, the tolerable minimum limits (of acetaldehyde) are not reached....".

U.S. Patent 4,064,112 describes a method for overcoming sticking problems during the solid stating process. It discusses the disadvantages of a solely

- 5 -

melt phase process and states that "elevated concentrations of acetaldehyde are to be expected in the melt."

U.S. Patent 4,362,852 describes devolatilizing molten polyamide or polyester polymers with a rotary disk processor. The disk pack is located very close to the spin block in order to minimize polymer degradation during spinning of fibers.

U.S. Patent 4,836,767 describes a method to reduce acetaldehyde during molding. It states that acetaldehyde increases linearly with time and exponentially with temperature.

Japan Patent Application 55-069618 (1980) states that PET with an acetaldehyde content less than 20 ppm is obtained by melt polymerization followed by extrusion into fiber or film and subsequently passing the fiber or film through a fluid or vacuum. Fluids used included air, nitrogen, water and steam.

U.S. Patents 5,119,170 and 5,090,134 mention the necessity of solid stating PET polymers in order to obtain low acetaldehyde concentrations.

U.S. Patent 4,963,644 describes the various reasons for solid stating of PET polymers.

U.S. Patent 4,591,629 states that melt phase produced PET has an unacceptably high level of acetaldehyde and uses solid stating in the presence of water to produce low levels of acetaldehyde.

U.S. Patent 4,230,819 describes the removal of acetaldehyde from crystalline PET with a dry gas (air or nitrogen at 170-250°C). It states that acetaldehyde cannot be completely removed from PET by heating it under reduced pressure.

It has also been disclosed in the art that additives may be used for reducing the acetaldehyde levels in PET.

- 6 -

U.S. Patent 5,102,594 describes supplying a thermoplastic condensation polymer such as PET in powder form to a vented extruder in which the polymer is devolatilized and then melted.

5 U.S. Patent 4,980,105 describes the devolatilization of polycarbonates in an extruder to remove volatiles (especially cyclic dimer) and then the melt is forced through a die.

10 U.S. Patent 4,255,295 describes a process for reclaiming waste polymer.

U.S. Patent 3,486,864 describes a polymerization reactor in which a solid prepolymer is first melted and then a vacuum is used to remove volatile glycol products as fast as possible. Alternatively, it is suggested
15 that a gas be mixed with the prepolymer prior to heating and melting to entrain the liberated glycol during polycondensation.

U.S. Patent 3,913,796 describes a vent-type injection molding machine in which gases such as
20 moisture, air, and other volatiles can be effectively removed. An extrusion screw is used for heating the solid resin to a semi-molten state prior to the injection molding machine.

U.S. Patent 4,060,226 describes a vented injection
25 molding screw extruder, with means to vent gases and vapors from the screw barrel, to produce devolatilized plasticized materials such as nylon and other degradable materials. Oxygen is excluded by means of a check valve.

30 U.S. Patent 4,142,040 discloses a method of processing in the molten state a saturated polyester resin so as to minimize degradation to yield acetaldehyde. This patent discloses in column 4, lines 38 et seq., "inert gas is introduced through one
35 or more conduits 3 into the bottom of the hopper or

- 7 -

through one or more conduits 3a into the feeding zone (or both). The inert gas flushes essentially all air from the polyester as it advances through the initial part of the feeding zone."

5

Brief Description of the Drawings

Figure 1 is a flow diagram illustrating the process of the present invention.

Figure 2 is a schematic diagram illustrating a
10 vented extruder which may be used in the process of the present invention.

Description of the Invention

In accordance with the present invention, there is
15 provided a process for producing molded polyester articles having a low acetaldehyde content comprising the steps of

- a) reacting a glycol and a dicarboxylic acid in the melt phase to form a polyester having an
20 I.V. of 0.65-0.85, the glycol being selected from the class consisting of glycols having 2-10 carbon atoms and the dicarboxylic acid being selected from alkyl dicarboxylic acids having 2-16 carbon atoms and aryl dicarboxylic
25 acids having 8-16 carbon atoms,
 - b) solidifying and pelletizing the polyester,
 - c) remelting the polyester, and
 - d) forming the polyester into shaped articles,
- wherein the molten polyester is devolatilized during or
30 following polymerization in the melt, during remelting, after remelting, or any combinations thereof by passing a purge gas over said molten polyester.

The polyester pellets may be crystallized by
conventional means known to those skilled in the art
35 (e.g., as disclosed in U.S. Patent 4,064,112) to improve

- 8 -

handling if desired, but in a manner so as not to increase molecular weight.

Polymers that are particularly useful in this process include poly(ethylene terephthalate),
5 poly(ethylene naphthalenedicarboxylate), and copolyesters containing up to 50 mol % of modifying dibasic acids and/or glycols. Modifying dibasic acids may contain from 2 to 40 carbon atoms and include isophthalic, adipic, glutaric, azelaic, sebacic,
10 fumaric, dimer, cis- or trans-1,4-cyclohexane-dicarboxylic, the various isomers of naphthalenedicarboxylic acids and the like.

Highly useful naphthalenedicarboxylic acids include the 2,6-, 1,4-, 1,5-, or 2,7-isomers but the 1,2-, 1,3-,
15 1,6-, 1,7-, 1,8-, 2,3-, 2,4-, 2,5-, and/or 2,8-isomers may also be used. The dibasic acids may be used in acid form or as their esters such as the dimethyl esters for example.

Typical modifying glycols may contain from 3 to
20 10 carbon atoms and include propylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, diethylene glycol, 1,4-cyclohexanediol, 1,4-cyclohexanediol dimethanol, and the like. The 1,4-cyclohexanediol dimethanol may be in the cis or the trans form or as cis/trans
25 mixtures.

The polyesters of this invention are readily prepared using polycondensation reaction conditions well known in the art. Typical polyesterification catalysts which may be used include titanium alkoxides, dibutyl
30 tin dilaurate, and antimony oxide or antimony triacetate, used separately or in combination, optionally with zinc, manganese, or magnesium acetates or benzoates and/or other such catalyst materials as are well known to those skilled in the art. Phosphorus and
35 cobalt compounds may also optionally be present.

- 9 -

Although we prefer to use continuous polycondensation reactors, batch reactors operated in series may also be used.

Although we prefer to use the polyesters in this process in an unmodified form, other components such as nucleating agents, branching agents, colorants, pigments, fillers, antioxidants, ultraviolet light and heat stabilizers, impact modifiers and the like may be used if desired.

Following preparation of the polyester in the melt phase to an I.V. of 0.65-0.85 as described above, the polyester melt may be passed through a suitable filter to remove impurities, gels, etc. Filtering of polymer is accomplished by well known means.

Suitable purge agents are well known in the art and may be for example, an inert gas, reactive scavenger, etc. Nitrogen is preferred.

Next, the polyester preferably is transferred to a devolatilization device. The devolatilization device can be any apparatus known in the art for generating a large amount of surface area per unit volume and/or for rapidly regenerating the exposed liquid surface. The devolatilization device should subject the liquid surface to a low partial pressure of acetaldehyde and volatile glycols either by using a purge agent or applied vacuum. The devolatilization apparatus may be a vented single-screw or twin-screw extruders (U.S. Patent 4,107,787), a vented twin-screw extruder (U.S. Patent 3,619,145), a rotating disk processor (DiscPac, cf. U.S. Patent 4,362,852), or device which generates thin films of polymer (cf. U.S. Patents 3,044,993, 3,161,710, and 3,678,983), and reactors having agitators with wire screens (U.S. Patent 3,526,484), or having agitators made of foraminous cages (U.S. Patent 3,279,895).

- 10 -

In the case of a high performance final polymerization reactor, a combination of equipment design, production rates, and operating conditions can facilitate increasing the molecular weight of the polyester and devolatilizing acetaldehyde in the same piece of equipment. In this advantageous embodiment, the polymer is rapidly pelletized via a gear pump linked directly to the exit of the reactor. In this embodiment, particular care must be taken to minimize the hold-up of polymer at the reactor exit and in the distribution lines going to extrusion heads. Suitable melt processing temperatures for poly(ethylene terephthalate) polymers will generally be in the range of 260 to 310°C. Of course, processing temperatures may be adjusted for other types of polyesters depending on the melting point, I.V. value and the like.

Following the devolatilization device, the molten polyester is solidified and pelletized by apparatus well known in the art. The pelletized polyester may be crystallized if desired, to lower the risk of sticking during subsequent handling. If crystallization is used, the apparatus and procedure described in U.S. Patent 4,064,112 may be used.

The pelletized polyester, whether amorphous or crystallized (as shown in broken lines in the diagram of Figure 1), is normally stored prior to remelting for subsequent molding into useful articles. Storage may be in a dry, controlled atmosphere so the pellets will not pick up moisture. As described herein, moisture contributes to formation of undesirable by-products. However, if the storage is not dry, the subsequent remelting will be done in such a way to provide a means to dry the material while melting.

Polyester pellets from storage are remelted by feeding them to an extruder, preferably vented, as

- 11 -

illustrated in Figure 2. In this device the polyester's I.V. is raised to 0.75-0.80 in the melt phase. Also, the volatile impurities such as acetaldehyde are reduced. The extruder may include a purge agent and/or vacuum vent for removal of volatiles such as acetaldehyde. Either a single or twin screw extruder may be used. The single screw illustrated in Figure 2 includes barrel 10, having screw 12 contained therein for rotation, thereby feeding polymer pellets from feed hopper 14 down the length of the barrel where they are melted, degassed and finally extruded from the end at 16. Vent 19 removes moisture as the pellets are heated and melted. Normally, the pressure at vents 18 and 19 can range from 0.0001 to 3 atmospheres. Preferably, a purge agent can be used at either vents 18 or 19 to assist in the removal of volatiles. If used, the purge agent may enter the barrel through fittings feeding in through openings 18 and 19 (not shown), using conventional means well known in the art. Also, optional vents 20 and 22 may be used. Suitable melt processing temperatures for poly(ethylene terephthalate) polymers will generally be in the range of 260 to 310°C. Of course, processing temperatures may be adjusted for other types of polyesters depending on the melting point, I.V. value and the like. The devolatilized polyester from this extruder is conveyed to a mold where it is formed into a useful article such as a bottle preform.

The term "I.V." used herein refers to the Inherent viscosity of the polymer, as determined by standard methods on a solution of 0.5 g of polymer dissolved in 100 mL of a mixture of phenol (60% by volume) and tetrachloroethane (40% by volume).

The residual acetaldehyde content of the molten polymer is measured as follows:

- 12 -

Extruded polyester samples are collected into dry ice to quench the melt. The polymer is then immediately chopped into granules and approximately 6 g is placed into vials with rubber lined caps. Vials are stored at
5 -40°C for no longer than three days before analysis. The samples are then ground in a Wiley mill to pass a 20 mesh screen and placed in gas chromatography desorption tubes. The acetaldehyde is desorbed from the polymer at 150°C for 10 minutes and quantified by gas
10 chromatography.

Examples

The following examples will further illustrate the invention: However it will be understood that they are
15 provided merely for illustrative purposes, and are not intended to limit the scope of the invention in any way. Examples 1-10 utilize a crystallization step. Examples 11-20 omit a crystallization step.

Example 1 - Filtered poly(ethylene terephthalate) (PET) modified with 3.5 mol % 1,4-cyclohexanedimethanol (a 30/70 mol % cis,trans- mixture) and with an I.V. = 0.64 is fed to a vented twin-screw reactor. After a residence time of 25 min at a temperature of 275°C and a pressure of 9.75 torr, the polymer has an I.V. = 0.75
20 and residual acetaldehyde of 5 ppm. The polymer is then pelletized through a pump and die system with less than 30 seconds average residence time. The amorphous pellets are crystallized in a Bepex crystallization unit at 120°C for 30 minutes. It is kept in dry storage
25 prior to being remelted and molded in a molding machine where the melted polymer has a residence time above 260°C of less than 90 seconds. The amount of residual acetaldehyde in the molded preforms is 9 ppm and the
30 I.V. of the polymer in the preform is 0.73.

- 13 -

Example 2 - The crystallized pellets of Example 1 are kept in storage in contact with ambient moisture. It is remelted in an extruder in which the melting zone is swept by a counter current flow of dry nitrogen and molded in a molding machine where the melted polymer has a residence time above 260°C of less than 90 seconds. The amount of residual acetaldehyde in the molded preforms is 9 ppm and the I.V. of the polymer is 0.73.

Example 3 - PET is prepared to an I.V. = 0.74 with a final melt temperature of 285°C, filtered, pelletized, and crystallized. The pellets are distributed to a plurality of devolatilizing vented extruders. Each stream has a flow rate equal to the capacity of one multi-cavity molding machine. The polymer entering the devolatilizing extruders contains 3000 ppm of water and 210 ppm residual acetaldehyde. The devolatilizers are purged with nitrogen. While in the devolatilizer for a mean residence time of 15 min, the polymer is processed at 270°C. The polymer exiting the devolatilizer has 2 ppm residual acetaldehyde, and is ejected directly to a multi-cavity molding machine. The preforms produced have an I.V. = 0.77 and acetaldehyde = 5 ppm.

Example 4 - This example uses the same equipment configuration as Example 3. PET is prepared to an I.V. = 0.67 at 270°C in the melt-phase reactors, and it contains 60 ppm residual acetaldehyde after pelletization and crystallization for distribution to the devolatilizing extruders. After 10 min residence time in each devolatilizer under nitrogen purge, the polymer is molded into preforms with an I.V. = 0.70 and a residual acetaldehyde level of 3.5 ppm.

Example 5 - This example uses the same equipment configuration as Example 3. PET is prepared to an I.V. = 0.75 at 270°C in the melt-phase reactors, and it contains 80 ppm residual acetaldehyde after filtration,

- 14 -

pelletization, and crystallization. It is transported to and remelted in devolatilizing extruders. After 5 min residence time in each devolatilizer under nitrogen purge, and approximately 2 min traveling to the molds before being cooled, the polymer has an I.V. = 0.75 and a residual acetaldehyde content of 10 ppm. The acetaldehyde regeneration rate during the transport of the polymer out of the devolatilizer and through the molding machine to the molds is measured to be 1 ppm per minute.

Example 6 - PET is prepared to an I.V. = 0.71 at a temperature of 275°C, and is filtered, pelletized, and crystallized prior to transport to a devolatilizer\ reactor operating at 275°C and at 0.75 torr pressure. After a residence time of 10 minutes at 275°C where residual acetaldehyde is reduced to 6 ppm, a gear pump is used to pump the polymer through a distribution system to a plurality of multi-cavity molding machines. The resulting preforms have an I.V. = 0.75 and a residual acetaldehyde level of 10 ppm.

Example 7 - PET is prepared to an I.V. = 0.5 at 275°C, and pumped through filters to another polycondensation reactor operating at 275°C and 0.75 torr. This reactor generates a large amount of surface area and the polymer achieves an I.V. = 0.75 in 30 min. The molten polymer with 20 ppm acetaldehyde is pelletized, crystallized, and stored under dry storage conditions. The dry pellets are remelted and then pumped through a multi-hole die to generate thin molten threads which fall through an open vessel purged with nitrogen gas. The molten polymer is then collected at the bottom of the vessel and distributed to a plurality of molding machines. The resulting preforms have an I.V. = 0.75 and a residual acetaldehyde level of 10 ppm.

Example 8 - PET is prepared to an I.V. = 0.5 at

- 15 -

275°C, and pumped through filters to another polycondensation reactor operating at 275°C and 0.75 torr. This reactor generates a large amount of surface area and the polymer achieves an I.V. = 0.75 in 30 min.

5 The molten polymer with 20 ppm acetaldehyde is pelletized, crystallized, and stored. The pellets containing up to 5000 ppm moisture are remelted in a machine with a purged melting section and one vacuum devolatilization section with a 3 second average

10 residence time and then pumped through a multi-hole die to generate thin molten threads which fall through an open vessel purged with gas. The molten polymer is then collected at the bottom of the vessel and distributed to a plurality of molding machines. The resulting preforms

15 have an I.V. = 0.73 and a residual acetaldehyde content of 10 ppm.

Example 9 - PET is prepared to an I.V. = 0.64 by conventional technology with a final melt temperature of 285°C. After being pumped through a filter and then

20 pelletized and crystallized, the polymer contains 100 ppm residual acetaldehyde. The pellets containing acetaldehyde and moisture from ambient air contact are fed to a plurality of drying extruders feeding devolatilizing reactors. These reactor\devolatilizers

25 operate at 0.75 torr pressure and process the polymer to 275°C. After a residence time of 20 min, the polymer from each devolatilizer is pumped via a gear pump to a plurality of multi-cavity molding machines. An accumulation cavity for each molding machine is filled

30 sequentially via an appropriate switching valve and distribution lines. In this manner steady flow from the devolatilizer\extruder is maintained. The resulting preforms have an I.V. = 0.75 and a residual acetaldehyde content of 9 ppm.

- 16 -

Example 10 - PET is prepared to an I.V. = 0.64 by conventional technology with a final melt temperature of 285°C. After being pumped through a filter, pelletized, crystallized, and dried, the polymer contains 100 ppm residual acetaldehyde. The pellets are kept in dry storage. The pellets containing acetaldehyde are fed to a plurality of extruders feeding devolatilizing reactors. These reactor\devolatilizers operate at 0.75 torr pressure and process the polymer to 275°C. After a residence time of 20 min, the polymer from each devolatilizer is pumped via a gear pump to a plurality of multi-cavity molding machines. An accumulation cavity for each molding machine is filled sequentially via an appropriate switching valve and distribution lines. In this manner steady flow from the devolatilizer\extruder is maintained. The resulting preforms have an I.V. = 0.75 and a residual acetaldehyde content of 9 ppm.

Example 11 - Filtered poly(ethylene terephthalate) (PET) modified with 3.5 mol % 1,4-cyclohexanedimethanol (a 30/70 mol% *cis,trans*- mixture) and with an I.V. = 0.64 is fed to a vented twin-screw reactor. After a residence time of 25 min at a temperature of 275°C and a pressure of 0.75 torr, the polymer has an I.V. = 0.75 and residual acetaldehyde of 5 ppm. The polymer is then pelletized through a pump and die system with less than 30 seconds average residence time. It is kept in dry storage prior to being remelted and molded in a molding machine where the melted polymer has a residence time above 200°C of less than 90 seconds. The amount of residual acetaldehyde in the molded preforms is 9 ppm and the I.V. of the polymer in the preform is 0.73.

Example 12 - The pellets of Example 1 are kept in storage in contact with ambient moisture. It is remelted in an extruder in which the melting zone is

- 17 -

swept by a counter current flow of dry nitrogen and molded in a molding machine where the melted polymer has a residence time above 200°C of less than 90 seconds. The amount of residual acetaldehyde in the molded preforms is 9 ppm and the I.V. of the polymer is 0.73.

Example 13 - PET is prepared to an I.V. = 0.74 with a final melt temperature of 285°C, filtered, and pelletized. The pellets are distributed to a plurality of devolatilizing vented extruders. Each stream has a flow rate equal to the capacity of one multi-cavity molding machine. The polymer entering the devolatilizing extruders contains 3000 ppm of water and 210 ppm residual acetaldehyde. The devolatilizers are purged with nitrogen. While in the devolatilizer for a mean residence time of 15 min, the polymer is processed at 270°C. The polymer exiting the devolatilizer has 2 ppm residual acetaldehyde, and is ejected directly to a multi-cavity molding machine. The preforms produced have an I.V. = 0.77 and acetaldehyde = 5 ppm.

Example 14 - This example uses the same equipment configuration as Example 3. PET is prepared to an I.V. = 0.67 at 270°C in the melt-phase reactors, and it contains 60 ppm residual acetaldehyde after pelletization for distribution to the devolatilizing extruders. After 10 min residence time in each devolatilizer under nitrogen purge, the polymer is molded into preforms with an I.V. = 0.70 and a residual acetaldehyde level of 3.5 ppm.

Example 15 - This example uses the same equipment configuration as Example 3. PET is prepared to an I.V. = 0.75 at 270°C in the melt-phase reactors, and it contains 80 ppm residual acetaldehyde after filtration and pelletization. It is transported to and remelted in devolatilizing extruders. After 5 min residence time in each devolatilizer under nitrogen purge, and

- 18 -

approximately 2 min traveling to the molds before being cooled, the polymer has an I.V. = 0.75 and a residual acetaldehyde content of 10 ppm. The acetaldehyde regeneration rate during the transport of the polymer out of the devolatilizer and through the molding machine to the molds is measured to be 1 ppm per minute.

Example 16 - PET is prepared to an I.V. = 0.71 at a temperature of 275°C, and is filtered and pelletized prior to transport to a devolatilizer\reactor operating at 275°C and at 0.75 torr pressure. After a residence time of 10 minutes at 275°C where residual acetaldehyde is reduced to 6 ppm, a gear pump is used to pump the polymer through a distribution system to a plurality of multi-cavity molding machines. The resulting preforms have an I.V. = 0.75 and a residual acetaldehyde level of 10 ppm.

Example 17 - PET is prepared to an I.V. = 0.5 at 275°C, and pumped through filters to another polycondensation reactor operating at 275°C and 0.75 torr. This reactor generates a large amount of surface area and the polymer achieves an I.V. = 0.75 in 30 min. The molten polymer with 20 ppm acetaldehyde is pelletized and stored under dry storage conditions. The dry pellets are remelted and then pumped through a multi-hole die to generate thin molten threads which fall through an open vessel purged with nitrogen gas. The molten polymer is then collected at the bottom of the vessel and distributed to a plurality of molding machines. The resulting preforms have an I.V. = 0.75 and a residual acetaldehyde level of 10 ppm.

Example 18 - PET is prepared to an I.V. = 0.5 at 275°C, and pumped through filters to another polycondensation reactor operating at 275°C and 0.75 torr. This reactor generates a large amount of surface area and the polymer achieves an I.V. = 0.75 in 30 min.

- 19 -

The molten polymer with 20 ppm acetaldehyde is pelletized and stored. The pellets containing up to 5000 ppm moisture are remelted in a machine with a purged melting section and one vacuum devolatilization section with a 3 second average residence time and then pumped through a multi-hole die to generate thin molten threads which fall through an open vessel purged with gas. The molten polymer is then collected at the bottom of the vessel and distributed to a plurality of molding machines. The resulting preforms have an I.V. = 0.73 and a residual acetaldehyde content of 10 ppm.

Example 19 - PET is prepared to an I.V. = 0.64 by conventional technology with a final melt temperature of 285°C. After being pumped through a filter and pelletized, the polymer contains 100 ppm residual acetaldehyde. The pellets containing acetaldehyde and moisture from ambient air contact are fed to a plurality of drying extruders feeding devolatilizing reactors. These reactor\devolatilizers operate at 0.75 torr pressure and process the polymer to 275°C. After a residence time of 20 min, the polymer from each devolatilizer is pumped via a gear pump to a plurality of multi-cavity molding machines. An accumulation cavity for each molding machine is filled sequentially via an appropriate switching valve and distribution lines. In this manner steady flow from the devolatilizer\extruder is maintained. The resulting preforms have an I.V. = 0.75 and a residual acetaldehyde content of 9 ppm.

Example 20 - PET is prepared to an I.V. = 0.64 by conventional technology with a final melt temperature of 285°C. After being pumped through a filter, pelletized, and dewatered, the polymer contains 100 ppm residual acetaldehyde. The pellets are kept in dry storage. The pellets containing acetaldehyde are fed to a plurality

- 20 -

of extruders feeding devolatilizing reactors. These reactor\devolatilizers operate at 0.75 torr pressure and process the polymer to 275°C. After a residence time of 20 min, the polymer from each devolatilizer is pumped
5 via a gear pump to a plurality of multi-cavity molding machines. An accumulation cavity for each molding machine is filled sequentially via an appropriate switching valve and distribution lines. In this manner steady flow from the devolatilizer\extruder is
10 maintained. The resulting preforms have an I.V. = 0.75 and a residual acetaldehyde content of 9 ppm.

Unless otherwise specified, all parts, percentages, etc., are by weight.

The invention has been described in detail with
15 particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

- 21 -

CLAIMS

We claim:

- 5 1. A process for producing molded polyester articles having a low acetaldehyde content comprising the steps of
- 10 a) reacting a glycol and a dicarboxylic acid in the melt phase to form a polyester having an I.V. of 0.65-0.85, said glycol being selected from the class consisting of glycols having 2-10 carbon atoms and said dicarboxylic acid being selected from alkyl dicarboxylic acids having 2-16 carbon atoms and aryl dicarboxylic acids having 8-16 carbon atoms,
- 15 b) solidifying and pelletizing said polyester,
- c) remelting said polyester, and
- 20 d) forming said polyester into shaped articles, wherein the molten polyester is devolatilized by passing a purge agent over said molten polyester.
2. Process according to Claim 1 wherein the polyester from step a) has an I.V. of 0.70-0.80.
- 25 3. Process according to Claim 1 wherein said polyester is devolatilized in an extruder.
4. Process according to Claim 1 wherein the polyester has a final residual acetaldehyde content of less
- 30 than 10 ppm.
5. Process according to Claim 4 wherein the polyester has a final residual acetaldehyde content of less
- than 5 ppm.

35

- 22 -

6. Process according to Claim 1 wherein at least 80 mol % of said dicarboxylic acid is terephthalic acid or naphthalene dicarboxylic acid.
- 5 7. Process according to Claim 1 wherein at least 80 mol % of said glycol is ethylene glycol.
8. Process according to Claim 1 wherein said glycol is a mixture of ethylene glycol and cyclohexane-
10 dimethanol.
9. Process according to Claim 1 wherein said acid is terephthalic acid and said glycol is a mixture of 60-99 mol % ethylene glycol and 40-1 mol %
15 cyclohexanedimethanol.
10. A process according to Claim 1 wherein said polyester is crystallized prior to step c).
- 20 11. Process according to Claim 11 wherein the polyester is remelted and optionally dried and/or devolatilized in an extruder during and/or following remelting.

1/2

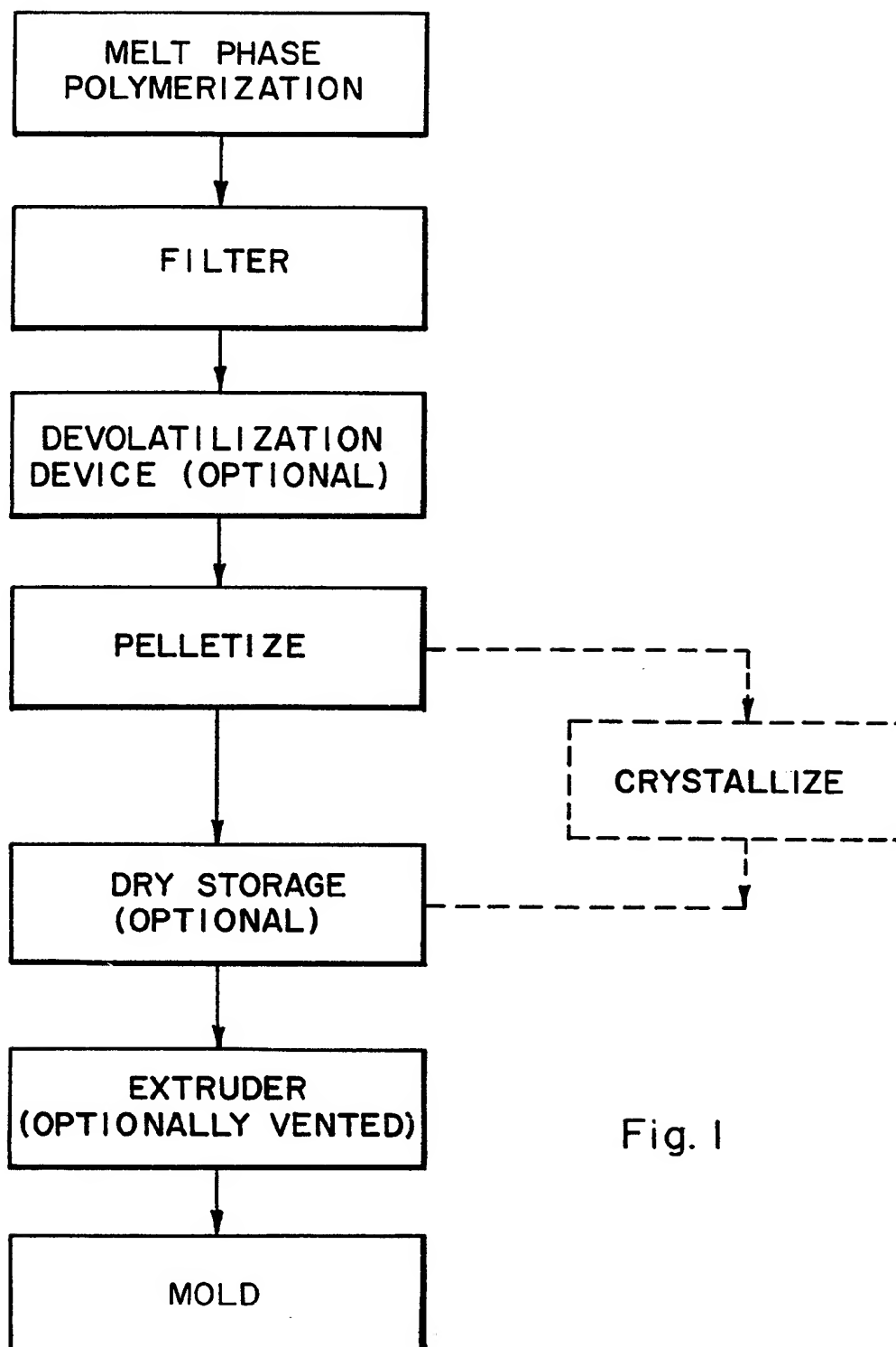


Fig. 1

2/2

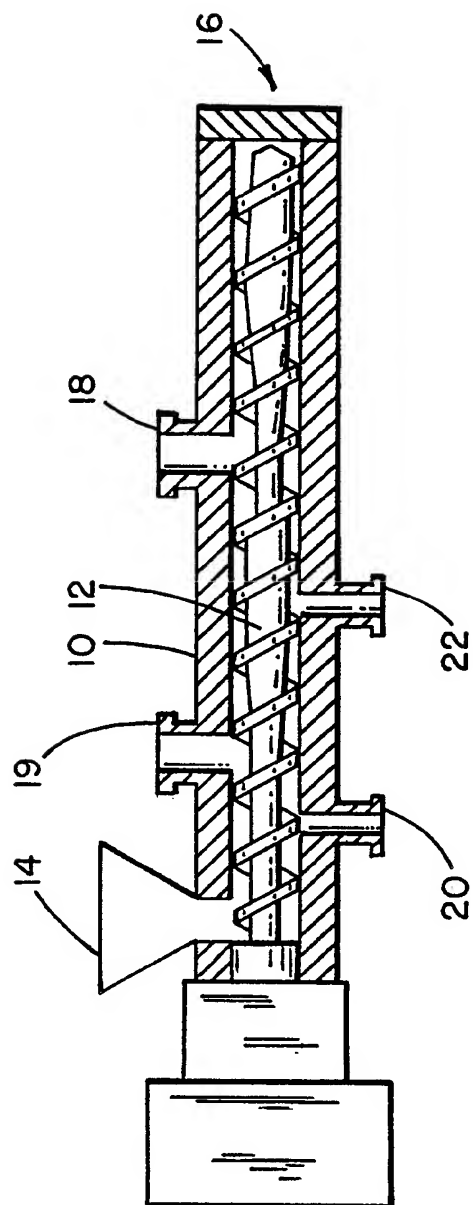


Fig. 2

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/12504

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G63/90

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A,4 142 040 (JABARIN ET AL.) 27 February 1979 cited in the application see column 3, line 17 - column 4, line 54; claims 1-4	1-11

Y	US,A,4 362 852 (PENDLEBURY ET AL.) 7 December 1982 cited in the application see claims 1-9 -----	1-11

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

11 November 1996

Date of mailing of the international search report

25. 11. 96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

Decocker, L

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/12504

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4142040	27-02-79	DE-A- 2907358 FR-A- 2423506 GB-A,B 2019424	25-10-79 16-11-79 31-10-79
US-A-4362852	07-12-82	NONE	